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XIX.

CONTRIBUTION TOWARDS THE HISTORY OF THE
FLUORIDES OF MANGANESE.

BY W. H. MELVILLE.

Presented by the Corresponding Secretary, June 14th, 1876.

THE investigation described in this paper was undertaken with a view to the re-examination of the fluorides of manganese. Many investigations have been made upon this subject during this century, and necessarily a large amount of fact has been accumulated.

* Berzelius noticed that, on the evaporation of a solution of manganous carbonate in hydrofluoric acid, ill-defined crystals were obtained, which dissolved in water only when containing an excess of acid. This amethyst-colored substance he called the proto-fluoride of manganese. He furthermore prepared a fluoride of manganese and potassium by double decomposition of a solution of manganous sulphate and fluoride of potassium. Similarly the soda salt was precipitated. These double fluorides were described as white precipitates, insoluble in water, and soluble in acids.

† When hydrated sesquioxide of manganese is dissolved in hydrofluoric acid and the solution left to evaporate spontaneously, dark brown prisms crystallize out, which dissolve completely in small quantities, but are decomposed by excess of water. When this decomposition ensues, a basic salt is deposited, while an acid salt remains in solution. A part of the former is redissolved on cooling, if free acid is present. Ammonia precipitates pure hydrated manganic oxide. (Berzelius.)

‡ A fluoride of manganese has been prepared, in which the Mn and F exist in the ratio 1 : 7 respectively. When a mixture of two parts potassic manganate or permanganate and one part fluor-spar is digested

* Gmelin, vol. iv. Manganese.

† Ibid.

‡ Wöhler, Pogg. 9, 619; Dumas, Ann. Chim. Phys., 36, 82.

with sulphuric acid in a platinum retort, a yellow vapor, purple in moist air, is evolved. This fluoride having the above ratio corrodes glass, and in so doing is resolved into (SiF_4) silicic fluoride and ($\text{H}_2\text{Mn}_2\text{O}_8$) permanganic acid. Chloride of calcium exposed to the yellow vapor evolves chlorine. The compound is absorbed by water, forming a purple solution, which contains hydrofluoric and permanganic acids. When the solution is evaporated in air, it evolves oxygen gas and hydrofluoric acid vapor, and leaves a brown residue from which water dissolves manganous fluoride, leaving a black insoluble basic salt. The solution dissolves copper, mercury, and silver, with formation of the corresponding fluorides.

* The tetrafluoride of manganese, MnF_4 , is produced in solution: (1) when hydrofluoric acid is allowed to act on an ethereal solution of MnCl_4 ; (2) when the acid acts on MnO_2 , in which case all the acid employed cannot be neutralized. The solution decolorizes indigo, and produces colors with anilin and naphthylamine; but may be preserved in the presence of glucose and gum-arabic. The substance dissolves in alcohol; decomposes in presence of much water, especially when it is alkaline, peroxide of manganese being formed. When potassic fluoride is added to the preceding solution, a rose precipitate is formed, which when dried at 100°C yields the formula $\text{MnF}_4 \cdot 2\text{KF}$. Ammonic fluoride yields a compound of analogous composition. The alkaline fluorides appear to give stability to the tetrafluoride. The potash salt melts, and after lengthened fusion the salt $\text{MnF}_2 \cdot 4\text{KF}$ is obtained. The solution of tetrafluoride precipitates an alcoholic solution of plumbic acetate. None of these compounds are crystalline. If to a boiling solution of potassic fluoride or ammonic fluoride perchloride of manganese is gradually added, a red powder comes down, the constitution of which is represented by the formula MnOF_2 . This oxyfluoride and the preceding tetrafluoride are soluble in anhydrous ether. Under the same conditions as above the sesquifluoride of manganese acts in a similar manner, the properties of the compounds thus formed being generally the same. With $\text{K}_2\text{Mn}_2\text{O}_8$ and hydrofluoric acid, either one or other of the following bodies is obtained: $\text{MnF}_4 \cdot 2\text{KF}$; $\text{Mn}_2\text{F}_2\text{O} + 2\text{KF}$.

† When MnO_2 is treated with hydrofluoric acid, brown crystals are sometimes deposited, especially when the mixture has been digested with the aid of heat. The crystals when dried on paper furnish the

* Bull. Chim. Soc. viii. 408, Nicklès.

† Ibid.

formula $\text{Mn}_3\text{F}_8 \cdot 10\text{H}_2\text{O}$. The substance is soluble in a small quantity of water, but decomposed by an excess into the brown oxide of manganese. Its solution forms a red precipitate with potassic fluoride. Dissolves silver, and is decolorized in passing to the state of proto-fluoride.

* A fluosilicate of Mn has been artificially prepared, represented by $\text{MnSiF}_6 \cdot 7\text{H}_2\text{O}$. Crystallizes in long six-sided prisms, and rhombohedrons. Color very light red. When heated, it first gives off seven molecules of water, then gaseous SiF_4 , leaving MnF_2 of the same form as the original crystals. Easily soluble in water.

Manganous Fluoride, MnF_2 .—Owing to the difficulty of obtaining manganous oxide free from higher oxides, it was found more practicable to prepare this fluoride by dissolving the white manganous carbonate in hydrofluoric acid. The resulting liquid was then evaporated on the water bath to dryness. The fluoride rendered anhydrous by drying at 100°C . gave by analysis:—

	Found.	At. Ratio.	Theory.
Mn	58.68	1.06	59.14
F ₂	40.57	2.13	40.86
	<hr/> 99.25		<hr/> 100.00

Manganese and fluorine were separated by decomposition with a concentrated solution of potassic hydrate, the hydrate of Mn thus formed converted into pyrophosphate, and the fluorine in the filtrate precipitated as calcic fluoride.

Properties.—Color white, shading faintly into pink. Structure crystalline, but indistinct. Insoluble, or sparingly soluble, in water and alcohol. Decomposed by the fixed alkalis and their carbonates. Dissolves in mineral acids, but in no case evolves hydrofluoric acid vapor except when treated with concentrated sulphuric acid. (It may be well to notice once for all that concentrated sulphuric acid invariably decomposes fluorides with evolution of hydrofluoric acid.) Dissolves in water containing free HF. Not decomposed by water, or by exposure to air. At red heat fuses to a dark brown mass with loss of fluorine.

Manganous Fluoride and Hydrofluoric Acid, $\text{MnF}_2 \cdot 3\text{HF} \cdot 9\text{H}_2\text{O}$.—When the anhydrous MnF_2 is dissolved in aqueous hydrofluoric acid, and the solution evaporated in vacuo over sulphuric acid, crystals containing free hydrofluoric acid are deposited. Also prepared directly

* Gmelin, vol. iv. Mn. Berzelius.

from manganous carbonate. The crystals freed from hygroscopic moisture gave the following numbers:—

	Found.	At. Ratio.	Theory.
Mn	17.90	.32	17.46
F ₅	29.16	1.54	30.16
H ₃			.96
9H ₂ O			51.42
			<hr/> 100.00

The salt was dissolved in water, the manganese precipitated with a solution of sodic carbonate, and, after filtration, fluorine was thrown down by calcic chloride.

Properties. — Colorless, sometimes light pink. Crystals are transparent long prisms of the trimetric system. Soluble in water, giving acid reaction. Soluble in acids. Effloresces in air; when heated at 100°C., changes into the simple MnF₂.

Double Fluoride of Manganous Oxide and Potassium, MnF₂. KF. — On the addition of an excess of potassic fluoride to a solution of manganous chloride, an immediate separation of an insoluble compound results. A double decomposition ensues, which is expressed by the reaction:—



The precipitate collected on a filter is washed with water, then with alcohol, and subsequently with ether. Alcohol and ether are employed to remove the last traces of water. Heating at 100° produces the same result:—

	Found.	At. Ratio.	Theory.
Mn	36.23	.66	36.40
K	26.06	.66	25.87
F ₃	37.71	1.98	37.73
	<hr/> 100.00		<hr/> 100.00

The method used in analysis was based upon the conversion of the double fluoride into a mixture of sulphates of manganese and potassium. The weight of the sulphates being known, as also that of the manganese therein contained, the percentages of the metals were easily calculated, while the fluorine was inferred by difference.

Properties. — Flesh colored. Crystalline. Insoluble in water and alcohol. Not decomposed in air and water. Dissolves in acids. Fuses at red heat.

This fluoride was first prepared by Gay-Lussac and Thenard, and afterwards described by Berzelius as a compound of manganese and potassium; but the latter established no ratio between the constituents.

An analysis of the soda salt which is precipitated under the same conditions will by analogy furnish the formula $\text{MnF}_2 \cdot \text{NaF}$.

Another double fluoride of manganese and potassium has been obtained by adding potassic fluoride to a solution of $\text{MnF}_2 \cdot 3\text{HF}$. A white crystalline precipitate is immediately thrown down, which analysis shows to contain Mn and K in the ratio 1 : 4 respectively. This double fluoride has identical properties with the preceding.

Tetrafluoride of Manganese, $\text{MnF}_4 \cdot 4\text{H}_2\text{O}$. — (1) A black oxide of manganese was prepared by exposing manganous carbonate to a dull red heat for a considerable time. This oxide was proved to be Mn_2O_3 : —

	Found.	At. Ratio.	Theory.
Mn_2	69.62	1.26	69.60
O_3	30.38	1.89	30.40
	<hr/> 100.00		<hr/> 100.00

This oxide dissolves readily in hydrofluoric acid with the aid of heat, and the deep red solution, when evaporated to the crystallizing point, deposits crystals on cooling. A larger crop of crystals is obtained by carrying the solution to dryness in vacuo. (2) Pure peroxide of manganese is dissolved in hydrofluoric acid under pressure with the aid of heat. On evaporating the solution red crystals are obtained.

In the following analysis, Mn was estimated, and the combined weight of fluorine and water inferred from the loss. The water was then determined in a second portion of the material by ignition with plumbic oxide. The fluorine was thus indirectly ascertained: —

	Found.	At. Ratio.	Theory.
Mn	27.22	.49	27.10
F_4	36.82	1.94	37.43
$4\text{H}_2\text{O}$	35.96	1.99	35.47
	<hr/> 100.00		<hr/> 100.00

Properties. — Color, red by reflected, purple by transmitted; light. Crystallizes in the monoclinic system in rather long, narrow prisms. These prisms consist in basal planes at the end of the ortho and kline

diagonals, and in four planes constituting a vertical dome; they terminate at one end in two planes which form one-half of a kline dome. Partially decomposed by large quantities of water and alcohol; completely by a solution of a fixed alkali into the brown hydrate of manganese and fluoride of the alkali. Soluble in acids; partially soluble in anhydrous ether. Insoluble in benzol and toluol. When the solution of this fluoride before crystallization is boiled, a dark brown substance is deposited, which evolves HF vapor with sulphuric acid. The crystals retain their crystalline form, but turn dark brown on exposure to air or the temperature of 100°C . This brown substance is probably an oxyfluoride, in which two or a multiple of two atoms of fluoride in the original fluoride are replaced respectively by one or more atoms of oxygen.

I can account for the formation of MnF_4 instead of Mn_2F_6 from the sesquioxide in no way except by assuming either that during the process of evaporation the sesquifluoride breaks up into tetrafluoride, or that the existence of a sesquifluoride is impossible.

Double Fluoride of Peroxide of Manganese and Potassium, $\text{MnF}_4 \cdot 2\text{KF}$.—To a moderately concentrated solution of MnF_4 , potassic fluoride dissolved in water is added in excess. Care must be taken that the solution of potassic fluoride is concentrated, otherwise the tetrafluoride of manganese will be decomposed. A rose-colored precipitate immediately separates, which when dried at 100°C . presents the following composition:—

	Found.	At. Ratio.	Theory.
Mn	22.00	.40	22.25
K_2	31.82	.81	31.65
F_6	46.18	2.43	46.12
	<hr/> 100.00		<hr/> 100.02

The analysis was conducted in the same manner as that of the former double fluorides.

Properties.—Rose colored. Under the microscope exhibits traces of crystalline structure; form indistinct. Decomposed by water, but not so readily as the tetrafluoride. Soluble in acids. Stable in air. Fuses to a blue mass, which on cooling resumes its original color.

A fluoride of manganese was prepared, in which the ratio between manganese and fluorine was found to be 1 : 8 respectively. This fluoride, however, requires further study; and it is hoped that, if the above ratio shall be proved beyond question to exist, the exact relation and disposition of the atoms will be determined.

Finely pulverized $K_2Mn_2O_8$ was dissolved in aqueous hydrofluoric acid, and the solution subjected under pressure to the temperature of $100^\circ C$ two or three hours. The red solution was then evaporated in vacuo. Claret-red prisms belonging to the trimetric system were deposited, in which the ratio of the constituents — Mn, K, and F — was not determined. Consequently this substance also remains for future investigation.